SYNTHESIS, CHARACTERIZATION AND MODIFICATION OF METAL ORGANIC FRAMEWORK-235 FOR CARBON DIOXIDE ADSORPTION

By

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13557

Dissertation submitted in partial fulfillment of

the requirement for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

May 2014

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL)

Approved by,

_____

(Dr. Ghulam Murshid)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 201

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(Mohammad Asyraf bin Ibrahim)

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ABSTRACT

Reducing anthropogenic carbon dioxide (CO_2) emission and lowering the concentration of greenhouse gases in the atmosphere has quickly become one of the most urgent environmental issues in this era. There are both natural and human sources of CO_2 emissions. Natural sources include decomposition, ocean release, respiration and volcanoes. Human sources come from activities like cement production, deforestation and the burning of fossil fuels. Carbon capture and storage (CCS) from large point sources such as power plants is one option for reducing CO_2 emissions. While a variety of technologies and methods have been developed, the adsorption of CO_2 from gas streams is still a critical issue. Apart from establishing new techniques, the exploration of capture materials with high adsorption performance and low capital cost are of paramount importance. Metal-organic frameworks (MOFs), a new class of crystalline porous materials constructed by metal-containing nodes bonded to organic bridging ligand shows a great potential as adsorbents or membrane materials in gas separatation. Related with the title of the project, this project will focus on synthesis, characterization and modification of MOF-235 and it is believed can give impressive result in the adsorption ability of CO_2. Thus, MOF-235 can be a good alternative method in reducing CO_2 emission.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Scientific studies suggest that the incremented greenhouse gas concentrations in the atmosphere, particularly CO_2, are a major factor in global warming. For the first time in human history, the concentration of climate-warming CO_2 in the atmosphere has passed the milestone level of 400 parts per million (ppm). A report by 49 researchers from 10 countries said, "Global CO_2 emissions from burning fossil fuels will rise to a record 36 billion metric tons (39.683 billion tons) this year" (as cited in Reuters, 2013).

There are several methods to stabilize the CO_2 content in the atmosphere. For years the subject of CO_2 adsorption on Metal Organic Frameworks have been both challenged and fortified. Anbia, Hoseini et al (2012) suggested that a metal ion or cluster of metal ions and an organic molecule called a linker create a MOF compound represent a new class of porous crystalline materials that provide very high surface area and controllable pore size. The MOF-235 was first synthesized by Yaghi group in 2005. MOF-235 or [Fe3O (1,4-BDC)3 (DMF)3][FeCl4]·(DMF)3 is orange hexagonal single crystals in which each iron atom is trivalent. MOF-235 is built-up from corner-sharing octahedral iron trimers that are connected through linear terephthalic acid links.

Anbia and Hoseinie (2012) explained that grafting of amines onto surfaces of porous materials to enhance adsorption of the acidic CO_2 molecule is another strategy that has been applied to MOFs. Arstad et al. reported CO_2 adsorption isotherms on three new types of amine-functionalized MOFs. Adsorption capacities of up to 60 wt % were obtained. To date, several types of MOFs containing amino groups have been described in the scientific and patent literature.

1.2 Problem Statement

Considering the fact that CO_2 gas is one of the major contributor to the global warming, adsoprtion of CO_2 by using MOF-235 is one of the promising method to overcome this issue. Modification of MOF-235 by decorating the pores with amine functional groups to enhance CO_2 adsorption looks promising.

1.3 Objectives

In this project, there are several objectives that need to be fulfilled. They are:

1. To synthesis Iron Terephthalate, MOF-235 or [Fe3O (1,4-BDC)3 (DMF)3][FeCl4]·(DMF)3
2. To optimize and modify the MOF-235 by grafting of amines functional group into pores of MOF-235 to enhance adsorption of the CO_2 molecule
3. To characterize the structure of MOF-235 by using 4 methods which are:
    - Fourier Transform Infrared (FT-IR)
    - Brunauer–Emmett–Teller **(**BET)
    - Field Emission Scanning Electron Microscopy (FESEM)
    - Transmission Electron Microscopy (TEM)
4. To investigate the adsorption capacity of MOF-235 and AM-MOF-235 for CO_2

1.4 Scope of Study

Generally, in order to complete this project. Several scope of study need to be understood and it is related with the objectives. The first one is to identify the reagents and materials to synthesis the targeted MOF. MSDS sheets for each chemicals need to be understood. For the amine modification, an amine functional group will be reacted with the MOF-235 to create new compound. In this project, 2-amino-2-methyl-1-propanol (AMP) is used. Hence, the properties of the amine need to be study. To prove that the compound is generally been synthesized, characterization need to be done. Instruments that are suitable and effective for the characterization need to be identified. Manual for handling the instruments important to avoid any mistakes and to obtain precise results. Lastly, a correct method to obtain the adsorption capacity of the compound need to be found. Basically, a particular literature review research will cover all the scope of study.

CHAPTER 2
LITERATURE REVIEW

In chapter 2, the literatures are arranged properly and accordingly to make a clear understanding of the project. The literatures start from the sources of CO_2 in atmosphere to determine the largest contributor then each technology for capturing CO_2 is reviewed. Metal organic frameworks is discussed detailed for its special properties. Synthesis, characterization and modification of MOF are reviewed based on recent research papers.

2.1 Source of CO_2 Emission

CO_2 is an important long-lived trace gas in Earth's atmosphere currently comprising about 0.04% (400 parts per million) of the atmosphere on a molar basis. Despite its relatively small overall concentration, CO_2 is a potent greenhouse gas and plays a vital role in regulating Earth's surface temperature through radiative forcing and the greenhouse effect. In BBC article written by Mark Kinver highlights the concern about the CO_2 emission by Prof Le Quere said that "I am worried that the risks of dangerous climate change are too high on our current emissions trajectory." There are two major contributors of CO_2 emissons which are human sources and natural sources. Natural sources include decomposition, ocean release and respiration. Human sources come from activities like cement production, deforestation as well as the burning of fossil fuels like coal, oil and natural gas.

2.1.1 Human Sources

Human sources of CO_2 emissions are much smaller than natural emissions but they have upset the natural balance that existed for many thousands of years before the influence of humans. The reason is natural sinks remove around the same quantity of CO_2 from the atmosphere than are produced by natural sources. This had kept CO_2 levels balanced and in a safe range. But human sources of emissions have disturb the natural balance by adding extra CO_2 to the atmosphere without removing any. Figure 1 on the next page shows the percentages of human sources of CO_2 from the research by Le Quéré, C. et al. (2013). The global carbon budget 1959-2011. 87 percent of all human-produced CO_2 emissions come from the burning of fossil fuels

like coal, natural gas and oil. The remainder results from the clearing of forests and other land use changes (9%), as well as some industrial processes such as cement manufacturing (4%).

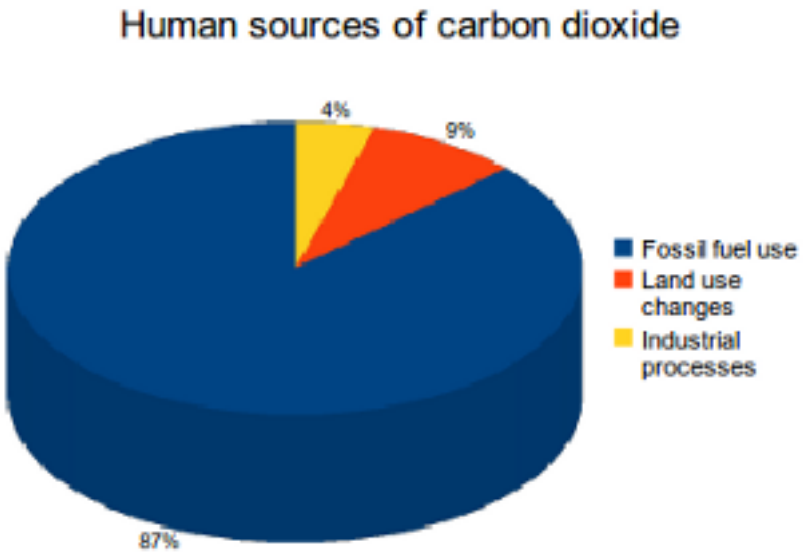

Figure 1: Human sources of CO_2 emissions

Based on research in 2011, 33.2 billlion tonnes of CO_2 is created from fossil fuel use worldwide. Coal is said been responsible for 43% of CO_2 emissions from fuel combustion which is the largest percentage compared to oil and natural gas which cover 36% and 20% respectively. It is approximately 2.5 tonnes of CO_2 produced for every tonne of coal burned. Coal represents one-third of fossil fuels' share of world total primary energy supply but is responsible for 43% of CO_2 emissions from fossil fuel use. Anything involving fossil fuels has a CO_2 emission ticket attached. So for example, burning these fuels releases energy but CO_2 also gets produced as a byproduct. This is because almost all the carbon that is stored in fossil fuels gets transformed to CO_2 during this process.

More detailed percentages from 87% of fossil fuel combustion is illustrated in figure 2 on the next page. This percentages is taken from CO_2 Emissions from Fuel Combustion (2012), International Energy Agency.

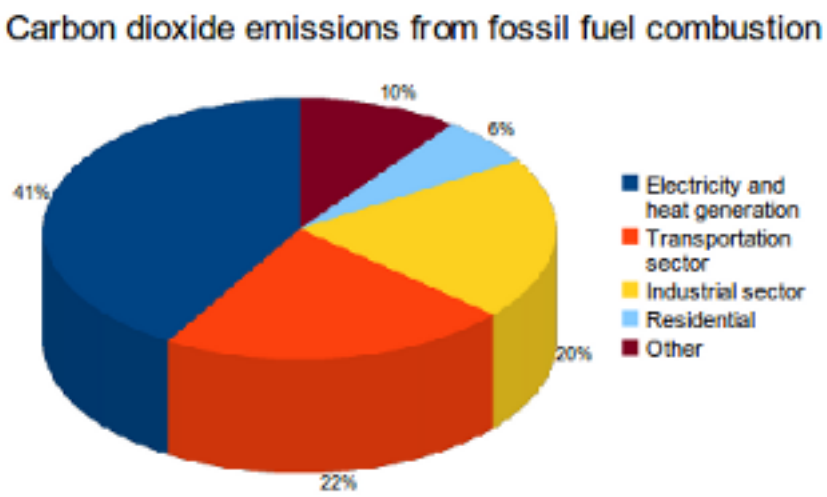

Figure 2: CO_2 emissions from fossile fuel combustion

2.1.2 Natural Sources

Apart from being created by human activities, natural processes also contribute to the releasing of CO_2 into the atmosphere (Gosselin, 2013). The Earth's oceans, soil, plants, animals and volcanoes are all natural sources of CO_2 emissions. Human sources of CO_2 are much smaller than natural emissions but they upset the balance in the carbon cycle that existed before the Industrial Revolution. The amount of CO_2 produced by natural sources is completely offset by natural carbon sinks and has been for thousands of years. Before the influence of humans, CO_2 levels were quite steady because of this natural balance. 42.84 percent of all naturally produced CO_2 emissions come from ocean-atmosphere exchange. Other important natural sources include plant and animal respiration (28.56%) as well as soil respiration and decomposition (28.56%). A minor amount is also created by volcanic eruptions (0.03%).

Figure 3 on the next page taken from IPCC Fourth Assessment Report: Climate Change 2007, Intergovernmental Panel on Climate Change shows the percentages of natural resources of CO_2.

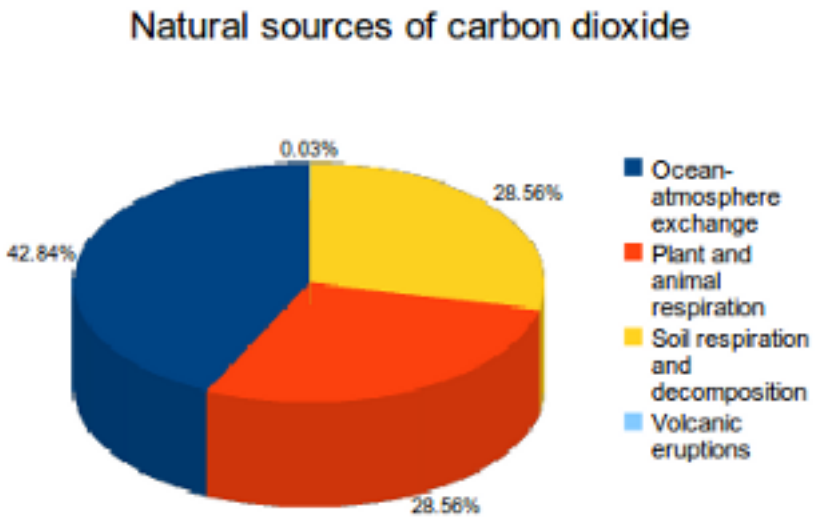

Figure 3: Natural souces of CO_2 emissions

2.2 Methods to Capture CO_2

According to (J. Rong Li et all, 2011), the most effective way to reduce CO_2 emission into the atmosphere is analysing cost effective and adaptable technologies for CO2 capture from the power generation and industrial fossil fuel combustion. Depending on the generation of CO_2, several capture options and tendentious technologies have been suggested and implemented. Two points must first be made with regards to capture materials and potential capture technologies, given the sheer magnitude of global CO_2 emissions. First, any chemical employed to capture CO_2 will rapidly exhaust its global supplies if it is used in a once-through manner and second any chemical produced from CO_2 as a reactant will rapidly saturate global markets for that chemical. These considerations underscore the necessity that capture materials must be regenerable.

In power plant, there are three basic CO_2 separation and capture options based on the fundamental chemical process involved in the combustion of fossil fuels which are as follows:

1. Post-combustion capture
2. Pre-combustion capture
3. Oxy-fuel combustion

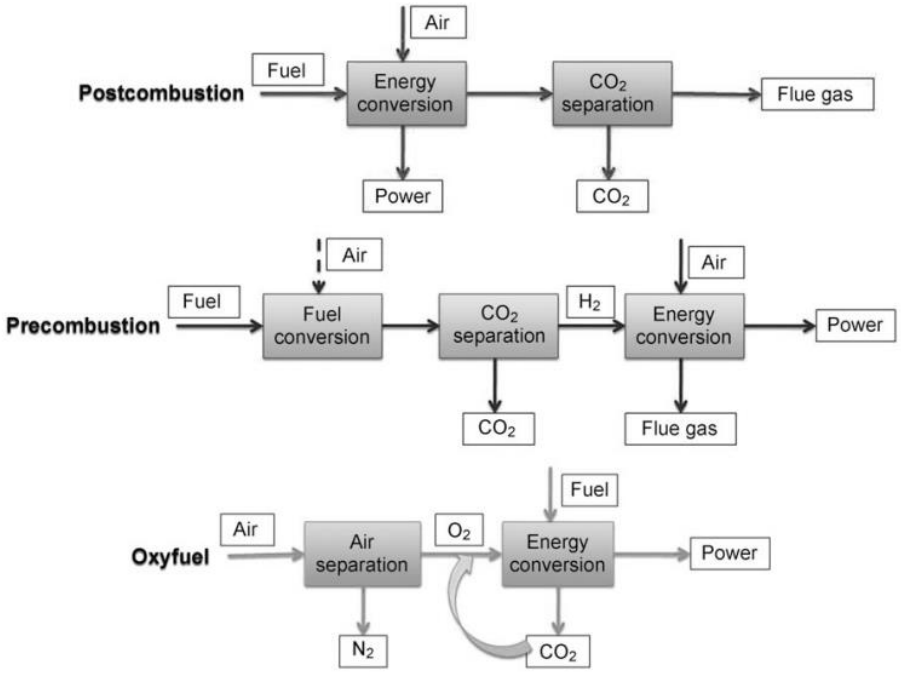

Figure 4: Three options for CO_2 capturing from power generation plants

Post-combustion "wet-scrubbing" CO_2 capture technologies have been employed industrially for over 50 years and are based predominantly on the industrially important primary alkanolamine MEA. The process involves the passage of an aqueous amine solution (typically 25–30 wt%) down the top of an absorption tower, while a gaseous stream of flue gas containing CO_2 is introduced at bottom. Post-combustion capture requires removing CO_2 from flue gas, comprised mainly of N2 and CO_2, before emission into the atmosphere. The most feasible on a short time scale is post-combustion capture because many of the proposed technologies can be retrofitted to existing fossil fuel consuming power plants. One such new approach involves also using cooled and CO_2-rich flue gases to feed bioreactors to produce microalgal biomass that would be used as a biofuel. An additional advantage of post-combustion capture is that even if when the CO_2 capture unit is shut down for an emergency, one can still generate electricity, which is not possible with the other more integrated capture methods. Post-combustion methods have been deployed commercially, primarily for the removal of minor contaminants such as Hg and SOx/NOx gas, but the materials for the CO_2 separation require modification, especially those with high preparation and regeneration costs.

While the retrofitting of existing power plants using post-combustion capture methods presents the closest marketable technology, two major alternatives to post-combustion. The emerging technologies of pre-combustion capture and oxyfuel processes are projected to attain higher efficiencies for CO_2 separation and capture which will compensate for their extensive capital investments in the longer term. Pre-combustion methods are employed in natural gas plants where CO_2 capture occurs at high partial pressures. The pre-combustion process for converting a methane rich fuel into hydrogen, for example, has given rise to Integrated Gasification Combined Cycle (IGCC) plant plants which involve three stages. Initially, a fuel (natural gas in this case) is reacted at high pressure and temperature to form a synthesis gas (syngas) containing CO, CO_2, and H_2. The second stage involves CO conversion using a water-gas shift reactor in which the CO_2 and hydrogen are separated prior to combustion. The significant advantage of pre-combustion capture is that the higher component concentrations and elevated pressures reduce the energy capture penalty of the process to 10–16%, roughly half that for post-combustion CO_2 capture. Although the initial fuel conversion steps are more elaborate and costly than in post-combustion systems, the high concentrations of CO_2 produced by the shift reactor (typically 15 to 60% by volume on a dry basis) and the high pressures often encountered in these applications are more favorable for CO_2 separation. A further advantage is that pre-combustion technology generates a hydrogen-rich fuel, which can be used as a chemical feedstock, in a fuel cell for power generation, or in the development of a hydrogen economy.

In contrast to post- and pre-combustion methods, oxyfuel combustion takes place in a pressurized CO_2-rich recirculating stream in which nitrogen is completely excluded from the combustion process through a preliminary air separation step. Suitable fuels include coal, natural gas, light to medium hydrocarbons or syngas (which could be derived from coal). The product of combustion is a concentrated stream of CO_2 (in high, sequestration ready concentrations of 80– 98%), which is circulated back into the system. The water product is removed from the flue gas by condensation. Oxyfuel technology forms the basis for “zero emission cycle” plants which are considered more promising for new installations compared with post-combustion CO_2 capture; however, the process requires significant redesign of the turbines, such that the retrofitting of existing plants is not considered economical.

Figure 5 schematically illustrates the technologies and method usually used in CO_2 separation; in each case, except for cryogenic separation, different materials are required as the carriers. Absorption (i.e. solvent scrubbing) is a well-established CO_2 separation approach used in the chemical and petroleum industries today. Absorption falls into two categories:

1. Physical, which is temperature and pressure dependent (absorption occurs at high pressures and low temperatures)
2. Chemical where absorption n of CO_2 depends on the acid–base neutralization reaction (in this case caustic solvents are required)

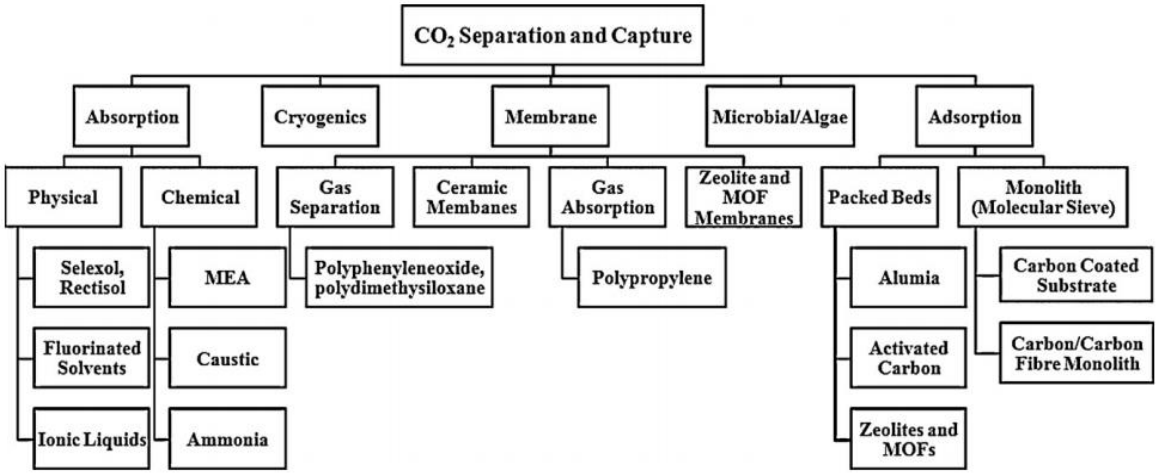

Figure 5: Different technologies and associated materials for CO_2 separation and capture.

Some of the preferred solvents are amines (such as monoethanolamine), ammonia solutions, Selexol, Rectisol, and fluorinated solvents. The most recent addition is ionic liquids, which have exhibited great potential. in absorption of CO_2 and are also environmentally benign. Cryogenic distillation uses a principle of separation based on cooling and condensation, and has been used in liquid separations or a long time. This technique is theoretically sound for CO_2 separation, however, the considerable energy demand deems it unreasonable for practical application. This method is more effective when the gas stream contains high CO_2 concentration and itcan be adopted in oxygen production for oxyfuel combustion. It is presently the most widely used system for the large-scale production of O_2 from the separation of air.

Membrane-based separation is based on the differences in physical and/or chemical interactions between gases and the membrane material, which can be modified to allow some components to pass preferentially through the membrane based on size (kinetic) and/or affinity (thermodynamics). Membranes have great potential in CO_2/H_2 separation in pre-combustion capture and post-combustion CO_2/N_2 separation. A wide variety of different membrane materials and processes are available, some of which already on an industrial scale, and potentially applicable in CO_2 separation. The performance and associated cost of these membrane-based technologies in large scale CO_2 capture mainly relies on the membrane materials themselves. Inorganic ceramic membranes and organic polymeric membranes have been used in CO_2 separation from flue gas in post-combustion. However, reaching a high degree of CO_2 separation by using single-stage ceramic or polymeric membrane is difficult as of yet (although it is feasible in terms of cost). New materials are still required to achieve the desired effectiveness in CO_2 separation by membranes.

Gas separation based on adsorption has been well developed, in which the selection of a sound adsorbent is the key for specific separation. Although materials for gas adsorptive separation have been established and a diverse range of useful sorbents are available for CO_2 separation, there is still plenty of room to optimize the performance of these materials and investigate a wider range of new sorbents. These adsorbents can then be combined with a broad range of process options yielding a fertile field for the optimization of separation performance. Conventional solid adsorbents include activated carbons, silica gel, ion-exchange resins, zeolites, and meso-porous silicates, activated alumina, metal oxides, and other surface-modified porous media. In recent years, a few of new adsorbents such as carbon fibres and their composites as well as metal-organic frameworks have been developed for gas separation. A recent review has comprehensively described the adsorbent materials for CO_2 capture from large anthropogenic point sources. Depending on the regeneration methods, several adsorption processes can been adopted to achieve CO_2 separation, including:

1. Vacuum and pressure swing adsorption (VSA and PSA)
2. Temperature swing adsorption (TSA)
3. Electric swing adsorption (ESA)
4. Simulated moving bed (SMB)
5. Purge displacement

Apart from physical and chemical methods mentioned above, biological methods have also been proposed for CO_2 separation. Algal bio-fixation of CO_2 in photo-bioreactors has, for example, recently gained great interest in CO_2 capture. In addition, attempts using chemoautotrophic microorganisms which use inorganic chemicals instead of light energy for CO_2 removal have also been investigated. It is evident that the progress and achievement of almost all of these technologies relies heavily on the development of materials. The challenges that arise in the development of these materials and techniques lies in being able to transfer the technology from the lab to the harsh conditions that it will be subjected to while maximizing efficiency and minimizing costs.

2.3 Metal Organic Frameworks

The last few decades have witnessed the extraordinary explosion of a new research of metal organic frameworks (MOFs). It is believed the first reports on MOFs date from the late 1950s and early 1960s although it was not until the end of the last century when Robson and co-workers, followed by Kitagawa et *all*., Yaghi and co-workers, and Ferey *et all*. retrieved and sustained the field. MOFs are actually crystalline compounds consisting of metal ions or clusters coordinated to rigid organic molecules to form one- two-, or three dimensional pore structures. What make these materials special are they hold very high adsorption capacities, specific surface areas and pore volumes in other word they are flexible materials**.**

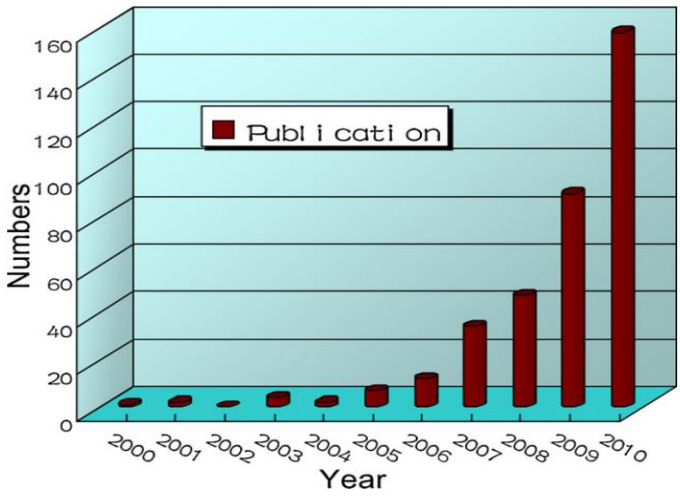

Figure 6: Publications on "CO_2 adsorption and/or separation in MOFs" per year showing the increasing research interest in this topic. Data from ISI Web of Knowledge, Thomson Reuter

There are several methods to synthesis MOFs. Solvent operations method is the most common method to create a crystal growth. Crystallization can be regarded as an equilibrium reaction between the dissolved precursors and the solid compound. The thermodynamic of this reaction at constant pressure is described with the Gibbs-Helmholtz equation (eqn (1)).

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

Besides, there are diffusion method, hydro(solvo)thermal method, microwave reaction and ultrasonic method. MOFs are formed by using transition-metal ions as nodes an multidentate organic ligands containing O- or N- donors as linkers [4,8]. In the syntheses of MOFs, the organic molecules give three different roles in the formation of various types of structures:

1. As a solvent for organic solvent
2. As a structure-directing agent
3. As a ligand to coordinate to the metal ion

There are reported that the synthesis and crystal structures of seven MOFs, [Cd(HBTC)2]2(HDETA)·4(H2O) (JUC-49), [Cd2(BTC)2(H2O)2]·2(HCHA)·2(EtOH)·2(H2O) (JUC-50), [Cd5(BTC)4Cl4]·4(HTEA)·2(H3O) (JUC-51), [Cd3(BTC)3(H2O)]·(HTEA)·2(H3O) (JUC-52), [Zn(BTC)(H2O)] (HTPA)·(H2O) (JUC-53), [Cd(BTC)]·(HTPA)·(H2O) (JUC-54), and [Cd2(BTC)(HBTC)]·(HTBA)·(H2O) (JUC-55), by using different organic amines as templates. Such amines include DETA, CHA, TEA, TPA, and TBA.

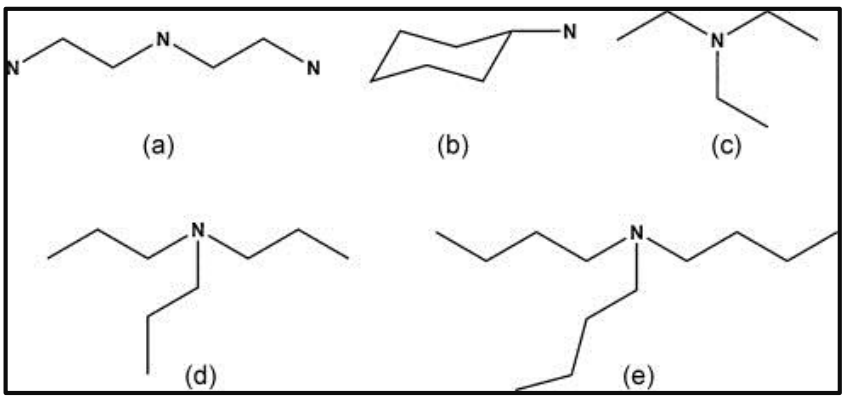

Figure 7: Representation of organic amines: (a) DETA, (b) CHA, (c) TEA, (d) TPA and (e) TBA

MOFs hold several records in porous materials including highest surface areas, hydrogen uptake based on physical adsorption, methane and CO_2 storage Recently, several thematic reviews have highlighted the rapid developments in the design, synthesis, and potential applications of these materials. As porous material, MOFs are therefore ideal adsorbents or membrane materials for gas storage and separation, including CO_2 capture due to their large surface areas, adjustable pore sizes, and controllable pore surface properties.

2.3 Modification of MOFs

The grafting of functional groups with a high affinity for CO_2 onto the surfaces of porous materials through ligand modification, or coordination to unsaturated metal centers has been employed as a strategy to enhance the capacity and selectivity for CO_2 adsorption. This approach has analogies with other functionalized solid adsorbents such as amine-grafted silica. However, the crystalline nature of metal–organic frameworks provides for a molecular level of control in tuning the gas separations properties. In view of the affinity of amines towards CO_2, amine-functionalized ligands have been incorporated into a number of frameworks in an attempt to enhance the selectivity and adsorption. An enhancement in the CO_2 uptake relative to CH_4 was observed for the flexible amino-MIL-53(Al) framework [Al(OH)(NH2bdc)] compared with the parent MIL- 53(Al) framework. Pulse chromatographic measurements revealed a separation factor of 60 for the functionalized material at low surface coverage, compared with ca. 5 for the parent framework. The magnitude of the zero-coverage adsorption enthalpy for CO_2 also increases from -20.1 to -38.4 kJ/mol upon functionalization. The incorporation of dangling amino groups reduces the number of a polar sites relative to the parent framework, resulting in negligible CH4 adsorption at pressures below 2 bar in the former case. Clearly, the presence of amino and OH groups drastically enhances the selectivity of the framework towards CO_2 adsorption. Similar enhancements have been reported in the amine-functionalized frameworks [Ni2(NH2bdc)2(dabco)] (dabco=1,4-diazabicyclo[2.2.2]octane) and [In(OH)- (NH2bdc)], relative to their non-functionalized analogs.

Alkylamine-functionalized frameworks have also been shown to enhance the selectivity for CO_2 adsorption, especially at the low pressures relevant to flue gas separation. Forexample, the air- and water-stable framework HCu[(Cu4Cl)- (BTTri)8] (H3BTTri=1,3,5-tri(1H-1,2,3-triazol-4-yl)benzene) contains exposed metal sites which can be reacted post-synthetically with diamines such as ethylenediamine (en). Clearly, extensive possibilities can be envisaged to tune the selectivity and heat of adsorption in amine-functionalized frameworks by incorporating secondary, tertiary or sterically hindered amines at open metal coordination sites, or on the bridging ligands. Such frameworks should overcome some limitations of other CO_2 capture materials, most notably:

1. The structural ambiguities present in hyperbranched aminosilica materials produced by surface polymerization
2. The lack of stability over multiple cycles for amine- impregnated silicas and zeolites

A study by Mansor Abia et all prove that with amine modification to MOF can increase the CO_2 adsorption capacities. Figure below illustrates the CO_2 adsorption capacities of MIL-101 (1) and PEHA-MIL-101 (2) at room temperature with various pressure.

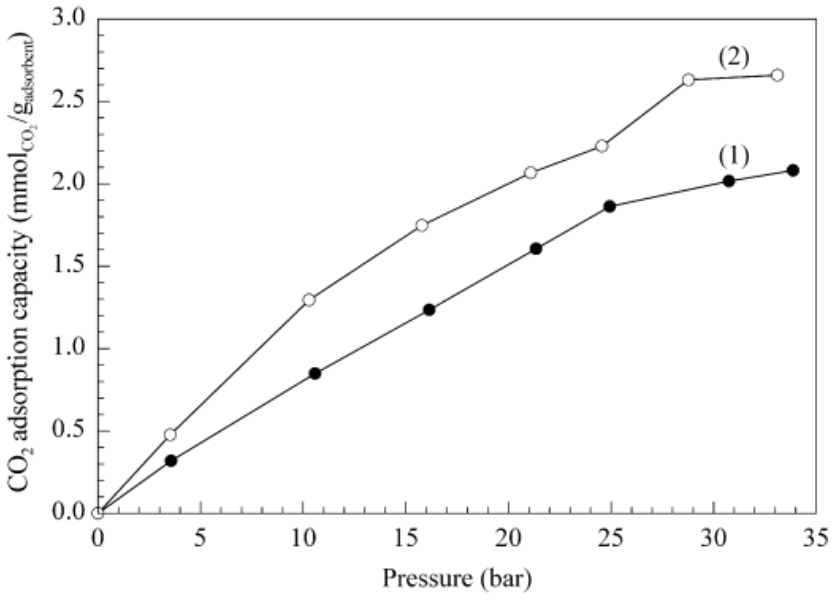

Figure 8: Graph of CO_2 adsorption capacity

2.4 Characterization of MOFs

For new MOFs, high-quality single crystals suitable for structural analysis are generally synthesized by slow reaction methods. But, for practical applications and for laboratory testing of adsorption properties, more rapid production may be desirable. Thus, faster solvothermal methods are applied for the synthesis of MOFs in larger quantities. In some cases, the products synthesized via these methods have shown rather different properties, compared to highly crystalline MOF materials that have been prepared via slow reaction methods.

There are several methods to characterize the MOFs. Recently used is single-crystal X-ray diffraction and powder X-ray diffraction (PXRD), along with an array of other techniques, to analyze the differences in the surface areas of different MOF-5-like samples. Another method to analyzed the large deviations in the surface areas of MOF-5-like materials using a combined small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) analysis and found a fractal network of aggregated mesopores that reduce the surface area and hydrogen uptake at room temperature.

Figure 9: XRD instrument

Because MOFs are crystalline, their surface areas can also be calculated geometrically from the corresponding crystal structures. There are several ways to do this, and, in a recent study, Duren et al. recommended that the “accessible surface area” is more appropriate for assessing adsorption behavior than the often-used Connolly

surface area. Other than that, Walton and Snurr simulated nitrogen isotherms in a series of MOFs and showed that the accessible surface areas agree very well with the Brunauer-Emmett-Teller (BET) surface areas obtained from the simulated isotherms. This demonstrates that the surface areas obtained using the BET method are physically meaningful. It also suggests that comparing the geometrically calculated accessible surface area with the BET surface area obtained from an experimental N_2 adsorption isotherm can provide a useful characterization of deviations in the sample from the perfect crystal structure. If the BET surface area is lower than the calculated accessible surface area, this could be due to the presence of reactants from the MOF synthesis, solvent molecules, partial collapse, or catenation.

Other methods to characterize the compound is Field Emission Scanning Electron Microscope (FESEM). A field-emission cathode in the electron gun of a scanning electronmicroscope provides narrower probing beams at low as well as high electronenergy, resulting in both improved spatial resolution and minimized samplecharging and damage. For applications which demand the highest magnification possible. Besides, Fourier transform infrared spectroscopy (FTIR) also been used to further characterize the newly synhesis compound. FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range.

Figure 10: FTIR Spectroscopy

CHAPTER 3
METHODOLOGY

3.1 Project Activities

Literature Review

- For FYP 2, further understanding on sythesizing and modifcation by using amine is done.
- More review on literature is done to understand the characterization method to analys the results.

Experiment

- Experiment is designed to synthesis MOF-235 and the modification by using amines.
- Chemicals and equipments required for the experiments are prepared and the synthesizing is done while modification is currently ongoing for the last sample.

Data Collection

- From the experiment conducted, the samples are withdrawn,
- Both samples of syhesizing and modification are analysed using 4 different characterization equipments.

Conclusion

- The project will be concluded based on the results at the end of the project.
- Report for the project will be prepared.

3.2 Gantt Chart and Key Milestone

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues															
2	Submission of Progress Report															
3	Project Work Continues															
4	Pre-SEDEX															
5	Submission of Draft Final Report															
6	Submission of Dissertation (Soft Bound)															
7	Submission of Technical Paper															
8	Viva															
9	Submission of Project Dissertation (Hard Bound)															

Process Suggested Milestone

Figure 11: FYP2 Gantt Chart and Key Milestone

3.3 Experiment Methodology

3.3.1 Synthesis of MOF-235

Substances and Chemicals

1. Terephtalic Acid ($C_8H_6O_4$)
2. Iron(III) Chloride Hexahydrate ($FeCl_3.6H_2O$)
3. Dimethylformamide (DMF)
4. Ethanol (C_2H_6O)

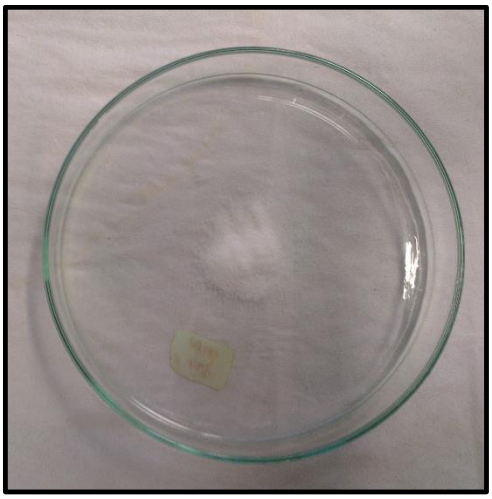

Figure 12: Terephtalic Acid ($C_8H_60_4$)

Figure 13: Iron(III) Chloride Hexahydrate (FeCl3.6H2O)

Experiment Procedures

1. An exact amount of $C_8H_6O_4$ (0.600 g) is weighted by using micro-balance and then mixed with 180 ml of DMF.
2. The mixture is stirred for 10 minutes by using magnetic stirrer until a clear solution is formed.
3. $FeCl_3.6H_2O$ is added into solution and then is stirred for another 5 minutes.
4. The reaction mixture of 180 ml and 180 ml of C_2H_6O are mixed together.
5. 360 ml of the mixture is loaded into Teflon-lined Autoclave and is placed in electic oven (85 °C) for 24 hours.
6. Orange powder of MOF-235 is collected and is washed by using DMF and Ethanol mixture for 3 times.
7. The product is dried overnight and is stored in glass vial.

Figure 14: Mixture of MOF-235, DMF and Ethanol

3.3.2 Modification of MOF-235

Substances and Chemicals

1. MOF-235 sample
2. Toluene (C_7H_8)
3. 2-amino-2-methyl-1-propanol (AMP)
4. Deionized Water
5. Ethanol (C_2H_6O)

Experiment Procedures

1. About 200 ml of Toluene and 5.00 g of AMP is added into the flask with 1.00 g of MOF-235 sample.
2. The contents of the glass are stirred at 400 rpm with 110 °C for 12 hours continuously.
3. The mixture is washed with DI water and ethanol by using vacum filtration until all AMP is washed out.
4. The product is dried overnight to yield AMP Modified MOF-235 and is stored in glass vial and named as AM-MOF-235.

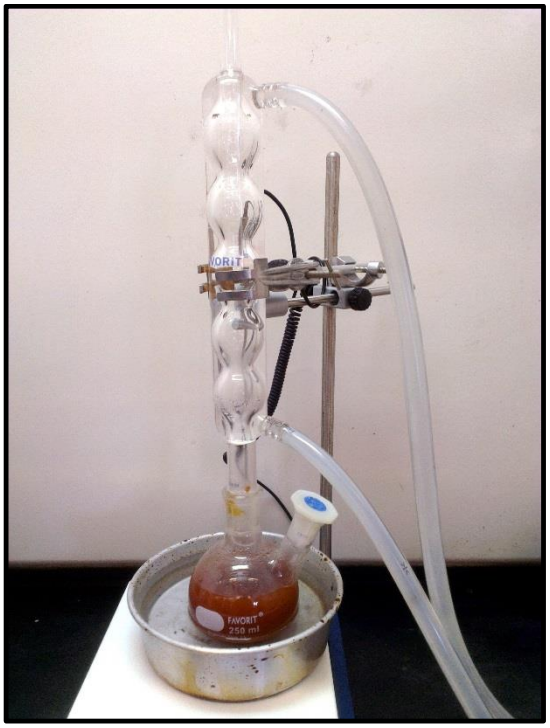

Figure 15: Equipment Setup for Modification

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Synthesis Results

MOF-235 is already been successfully synthesized based on methodology gained from the literature. Figure below showed the MOF-235 which is orange in colour and it is in powder form.

Figure 16: MOF-235

MOF-235 had been modified with AMP. Figure below shows MOF-235 that had been functionalized with AMP. It is also in powder form but it is a little bit rough compared to MOF-235. For easy labelling, it is named as AM-MOF-235.

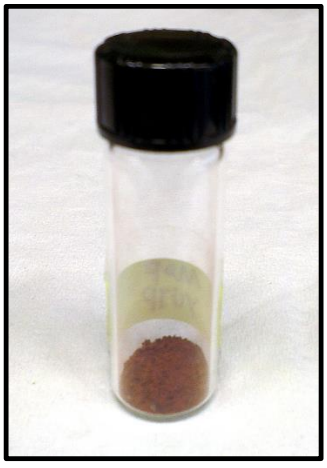

Figure 17: AM-MOF-235

4.2 Characterization Results

4.2.1 Fourier Transform InfraRed (FTIR) Analysis

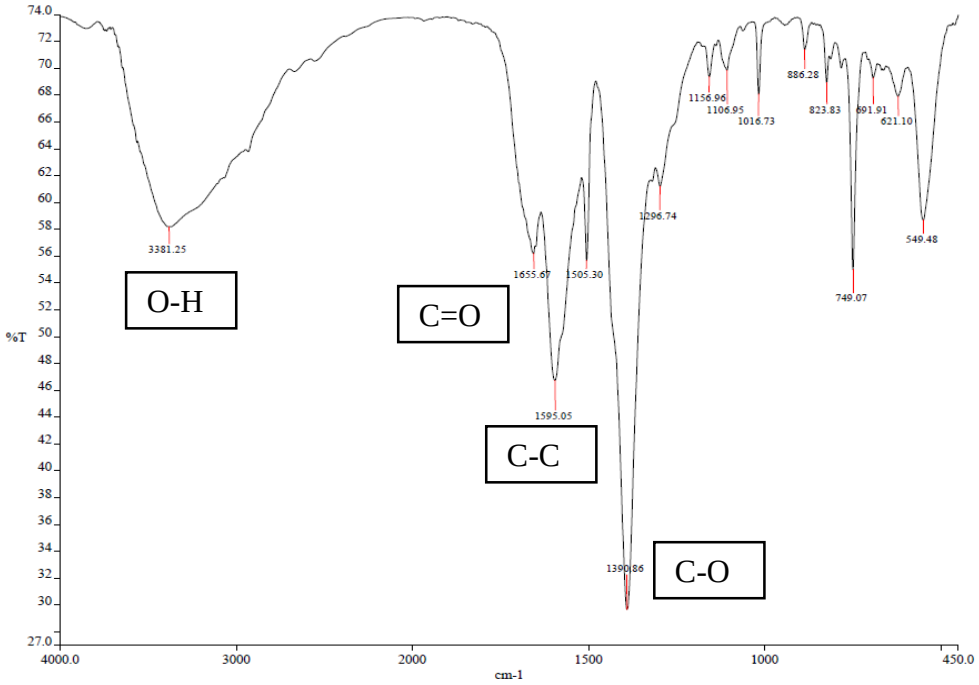

Figure 18: FTIR Spectra of MOF-235

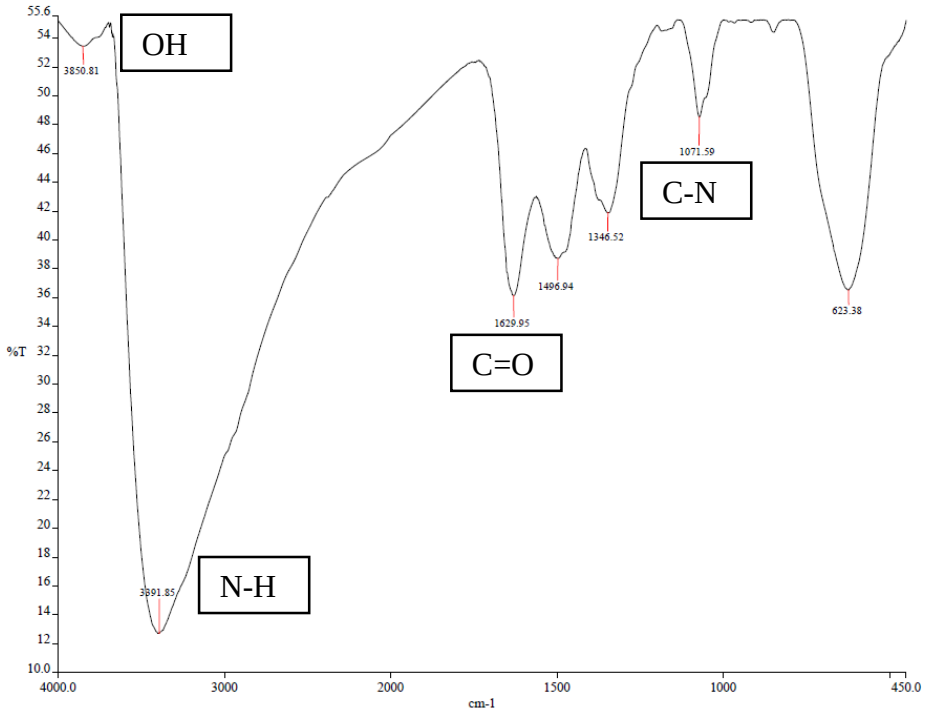

Figure 19: FTIR Spectra of AM-MOF-235

FTIR spectra of MOF-235 and AM-MOF-235 are shown in figure 18 and 19. The characteristic absorption peaks of the MOF-235 sample were observed at 1655.67, 1595.05, 1505.30, 1390.86, 1296.74 and 749.07 cm^{-1}, which could mainly originate from the carboxylate groups vibrations and are identical to those of reported data in the literatures. The broad peak centered at 3381.25 cm^{-1} is associated with the stretching vibrations of the O–H from the surface adsorbed water. This indicates the presence of alcohol functional group. The peak at 1595.05 cm^{-1} also can be related to the stretching vibrations of C-C bond of aromatic ring. The two sharp peaks at 1505.30 and 1390 cm^{-1} are assigned to asymmetric *(vas(C–O))* and symmetric *(vs(C–O))* vibrations of carboxyl groups, respectively, confirming the presence of the dicarboxylate linker within the sample. The peak at 749.07 cm^{-1} corresponds to C–H bending vibrations of the benzene. Therefore, the results of FTIR spectra clearly confirm the formation of MOF-235 structure. After modification with amine, 1 deep peak is appeared at 3391.85 cm^{-1} which can be related N-H stretching vibrations of amines. This confirms that the compound had been functionalized.

4.2.2 Transmission Electron Microscopy (TEM) Analysis

TEM analyses of samples prepared as described were performed at Central Analysis Lab (CAL) of Universiti Teknologi Petronas using Carl Zeiss AG - LIBRA 200 FE. Typically, TEM pictures of each sample were taken at 3 different magnifications. All TEM measurements were carried out under low dose conditions and at liquid nitrogen temperature using a GATAN cooling holder.

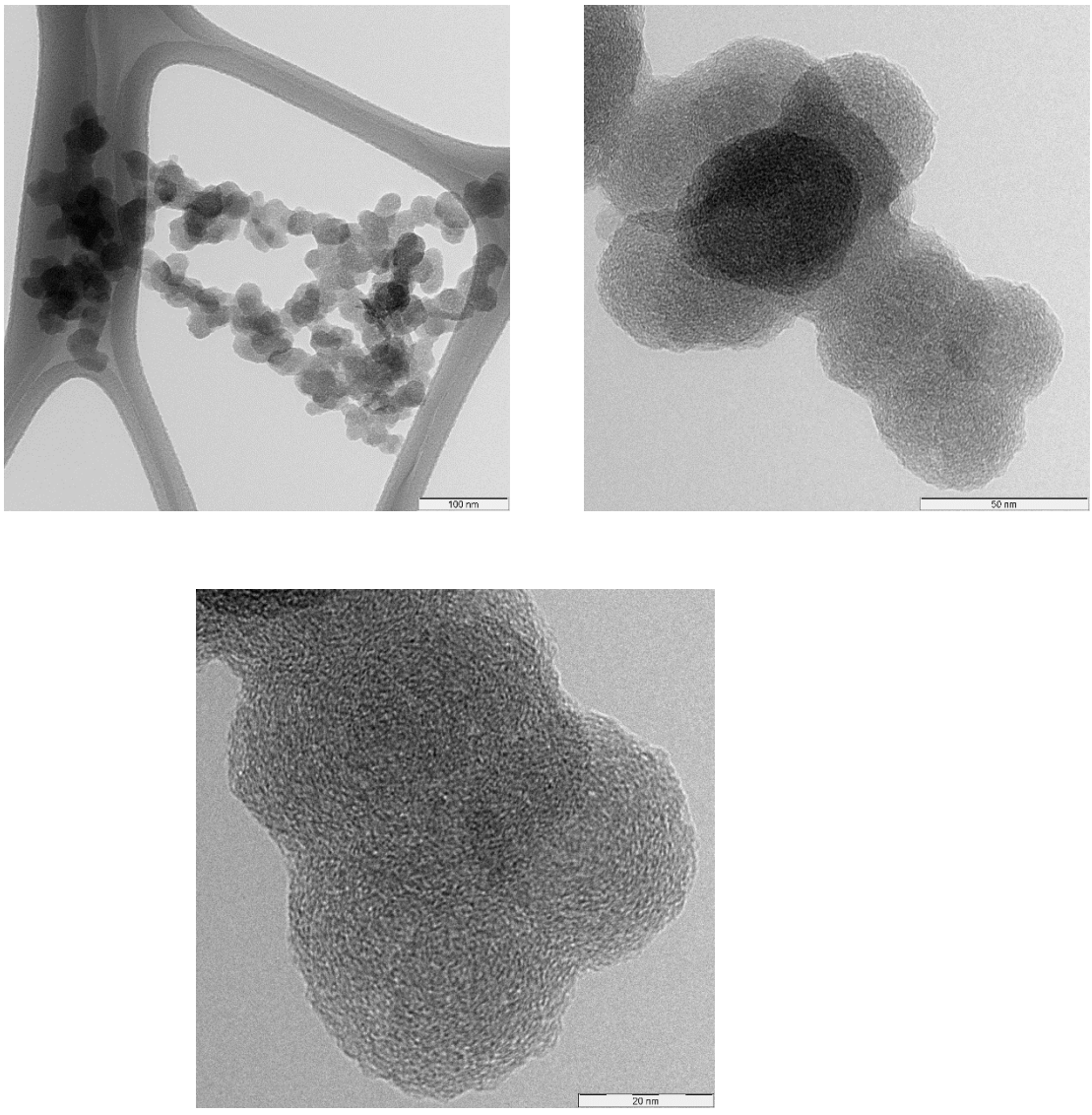

Figure 20: TEM images with 3 different magnifications of MOF-235

Transmission electron microscopy (TEM) examinations show the surface of the prepared MOF-235 powder (Figure 20). TEM image of the MOF-235, as shown in 20 at low magnification revealed nanosphere like crystal morphology with the dimension of particles 45–55 nm.. The places with darker contrast could be assigned to the presence of ferum chloride particles with different dispersion. Ordered arrangement of the pores was also seen from the high-resolution images. This result suggested quite uniform distribution of the framework elements.. In addition, the lattice line width is about 2-3 nm, suggesting that the MOF-235 sample has a high crystallinity.

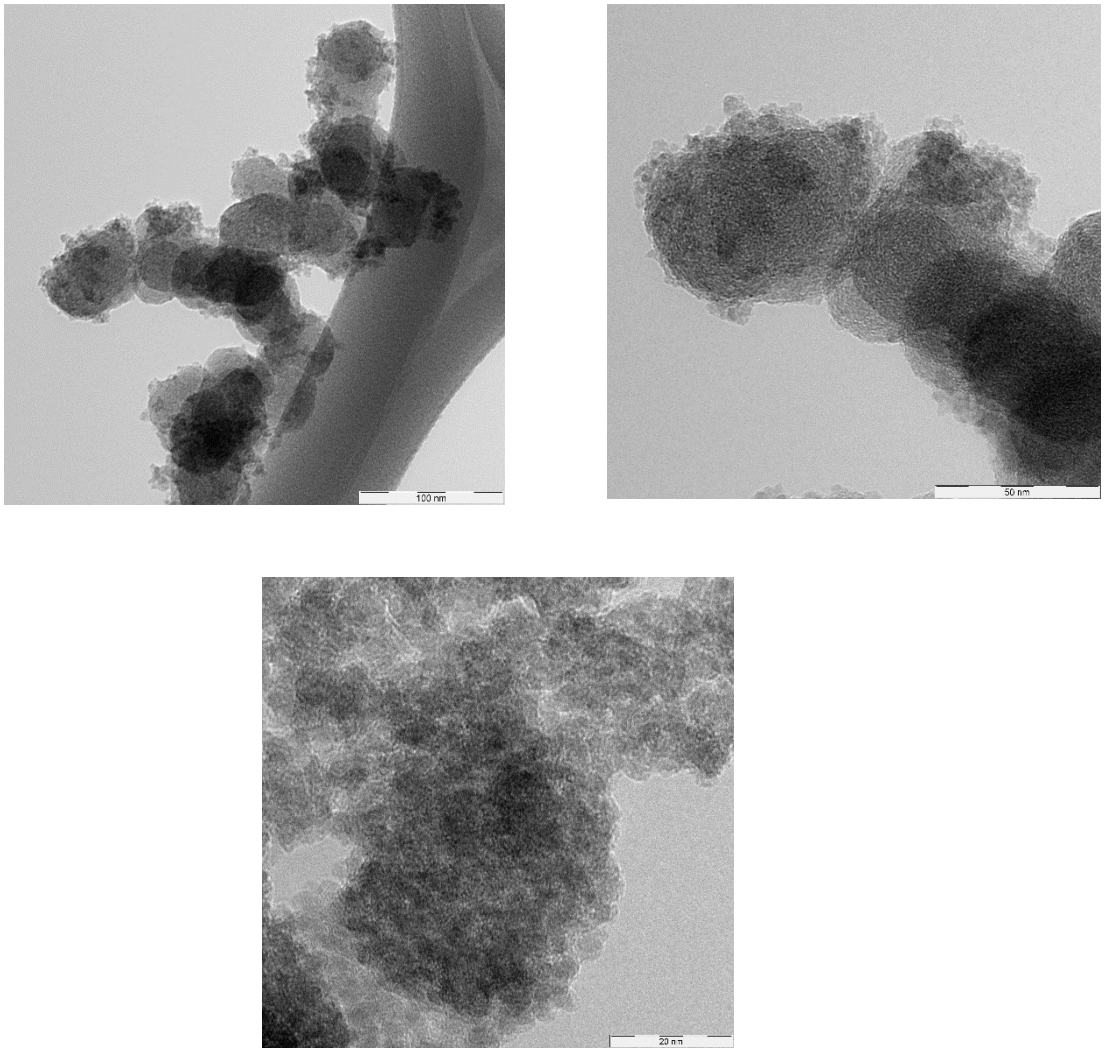

Figure 21: TEM images with 3 different magnifications of AM-MOF-235

While figure 21 shows the TEM images for AM-MOF-235 also with 3 different magnifications. Compared to images of MOF-235, AM-MOF-235 images look more tarnish and taint. Foreign substances are observed being attached at the edge of each molecules. This foreign substances could show the presence of amine into the material. . Moreover, the surface of MOF-235 looks very rough due to the agitation of reaction solution. Darker spots also could be assigned as the presence ferum chloride particles with different dispersion. The diameter of the particles remain same as MOF-235 with the range of 45–55 nm.

4.2.3 Field Emission Scanning Electron (FESEM)

FESEM analyses of samples prepared as described were performed at Central Analysis Lab (CAL) of Universiti Teknologi Petronas. A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage

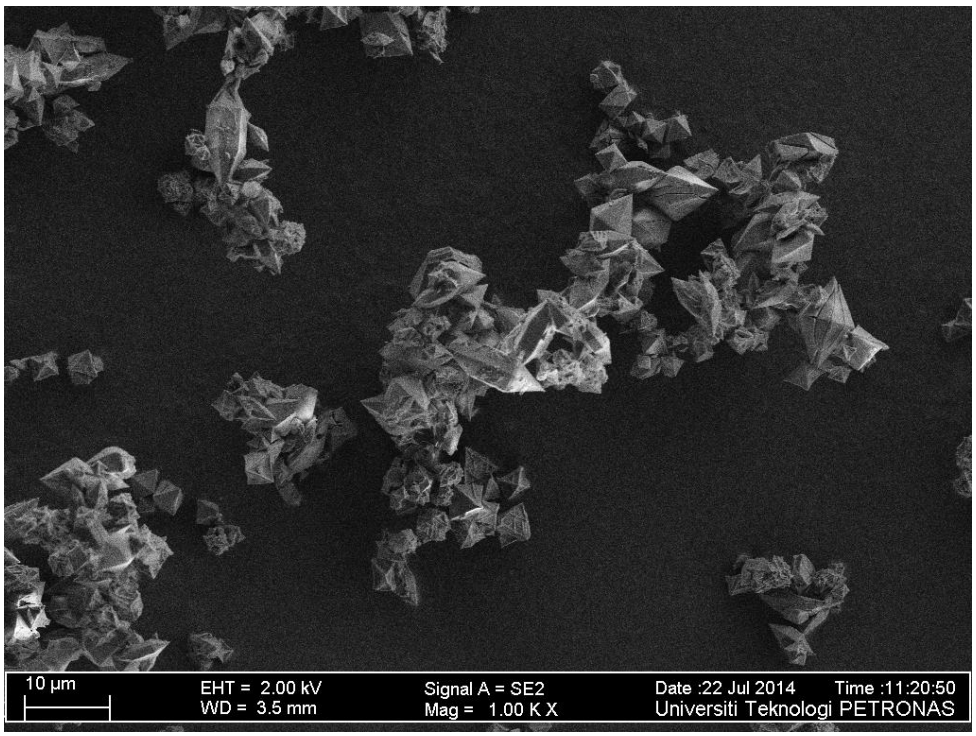

Figure 22: FESEM images of MOF-235 with 1.00 KX magnification

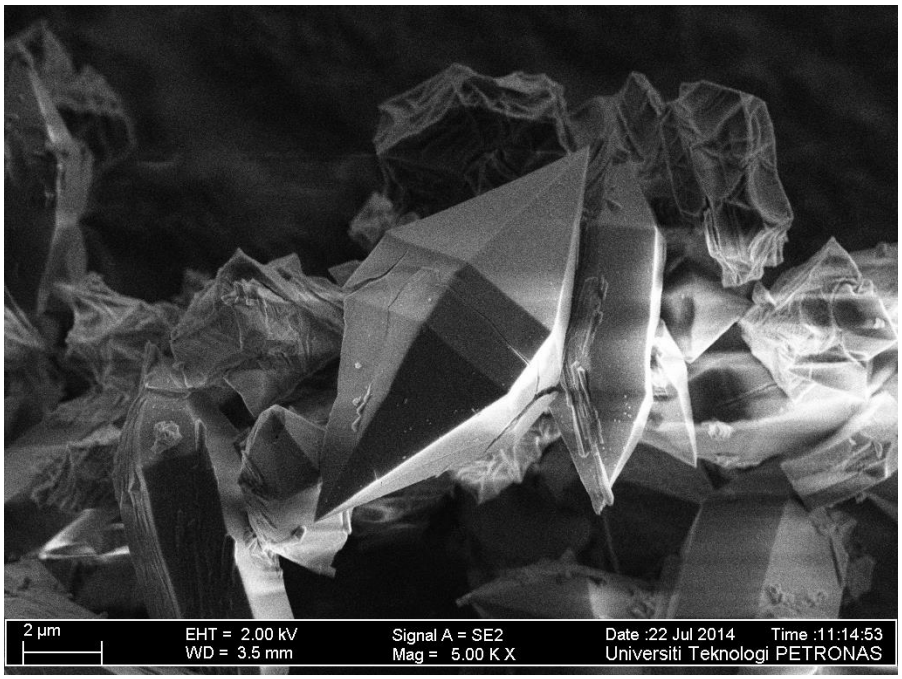

Figure 23: FESEM images of MOF-235 with 5.00 KX magnification

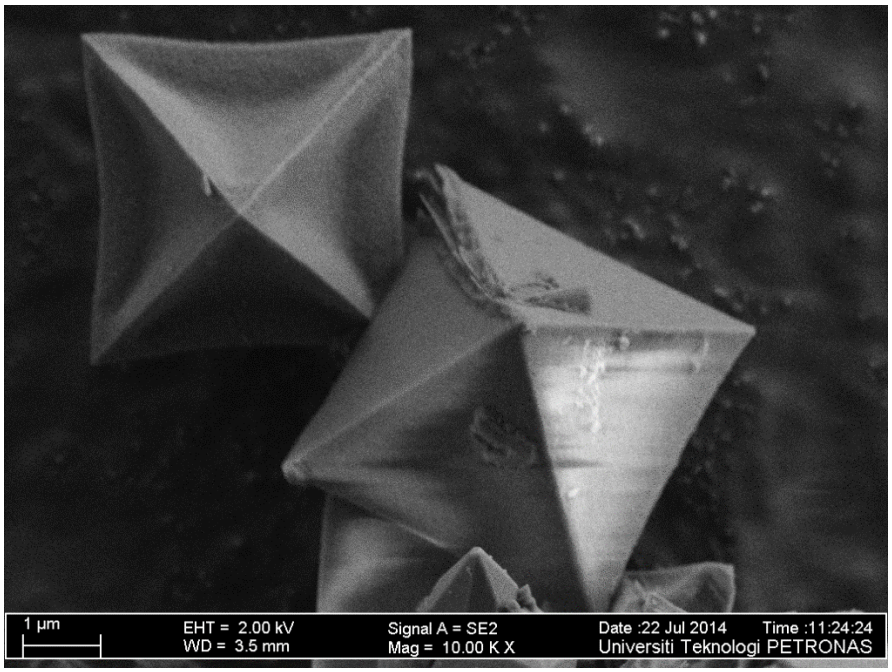

Figure 24: FESEM images of MOF-235 with 10.00 KX magnification

As expected, the FESEM micrograph showed that a crystalline material was achieved. From the images captured (Figure 22, 23 and 24), it is assumed that the particles have octahedron morphology. .It retains the basic octahedron structure, however many defects generate and the edges of the particles are much less sharp.

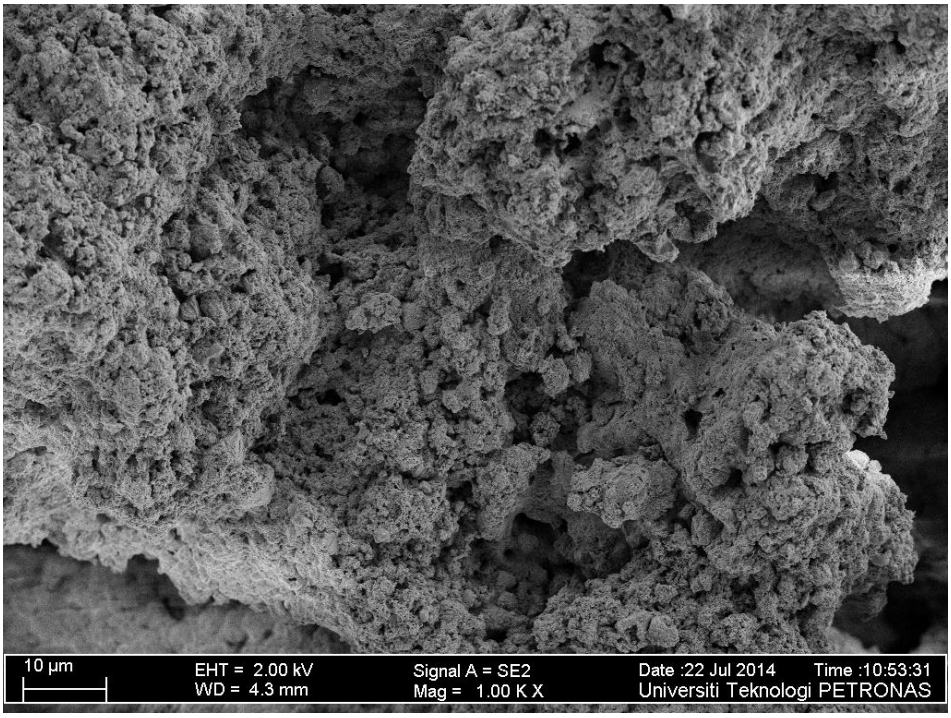

Figure 26: FESEM images of AM-MOF-235 with 1.00 KX magnification

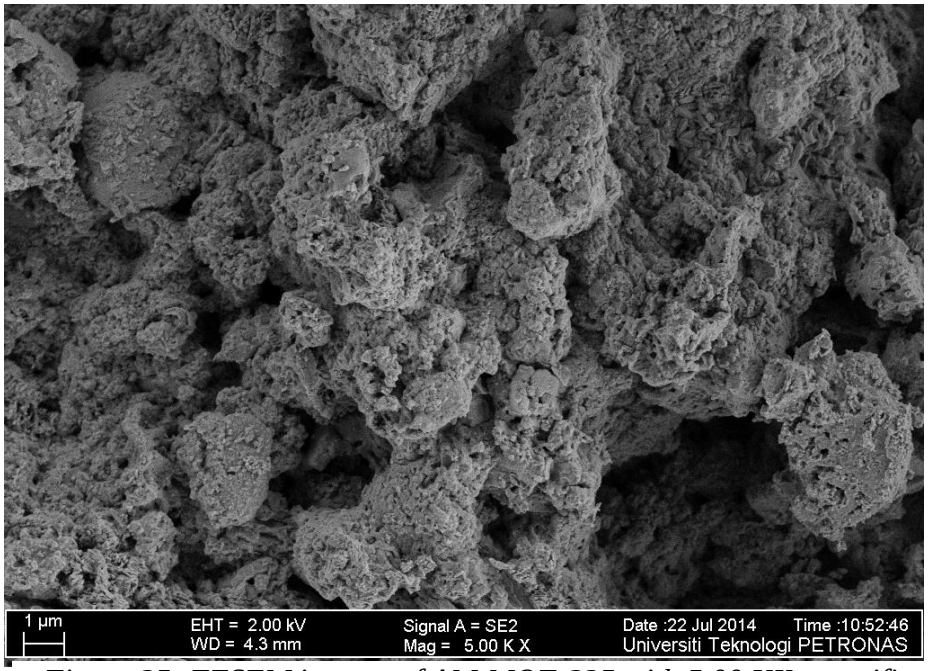

Figure 25: FESEM images of AM-MOF-235 with 5.00 KX magnification

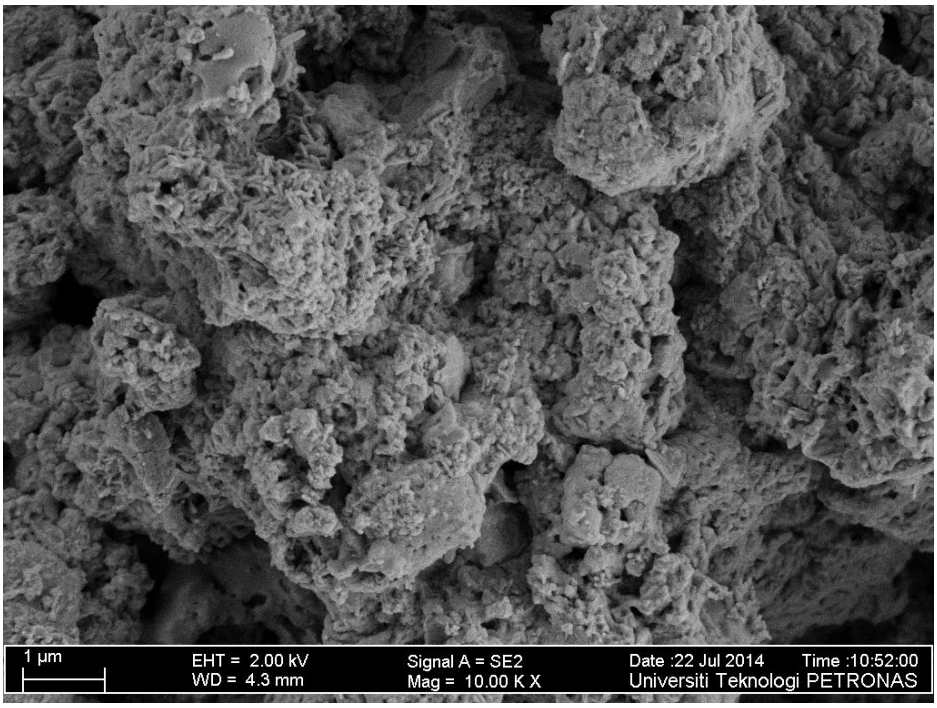

Figure 27: FESEM images of AM-MOF-235 with 10.00 KX magnification

The particle size of MOF-235 is much smaller than AMP-MOF-235, which confirms the hypothetical reason for higher surface area of MOF-235. . Many significant differences can be observed from the FESEM image of MOF-235 and AM-MOF-235. Compared to MOF-235, AM-MOF-235 did not show any clean crystal shape. It can be seen that there are some layer materials that must be embedded within the octahedron structure. Obviously these changes demonstrate that amine modification had fully change the structure of MOF-235 due to the presence of amino groups.

4.2.4 Brunauer Emmett Teller (BET) Analysis

The samples are being analysed at the Cental Analysis Lab (CAL) of Universiti Teknologi Petronas. BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser.

From the literature, MOF-235 has 974 m^2g^{-1} BET surface area while the pore volume is 0.93 cm^3g^{-1}. Due to some technical error happened at the analysis facilty. Only AM-MOF-235 gave out the result.

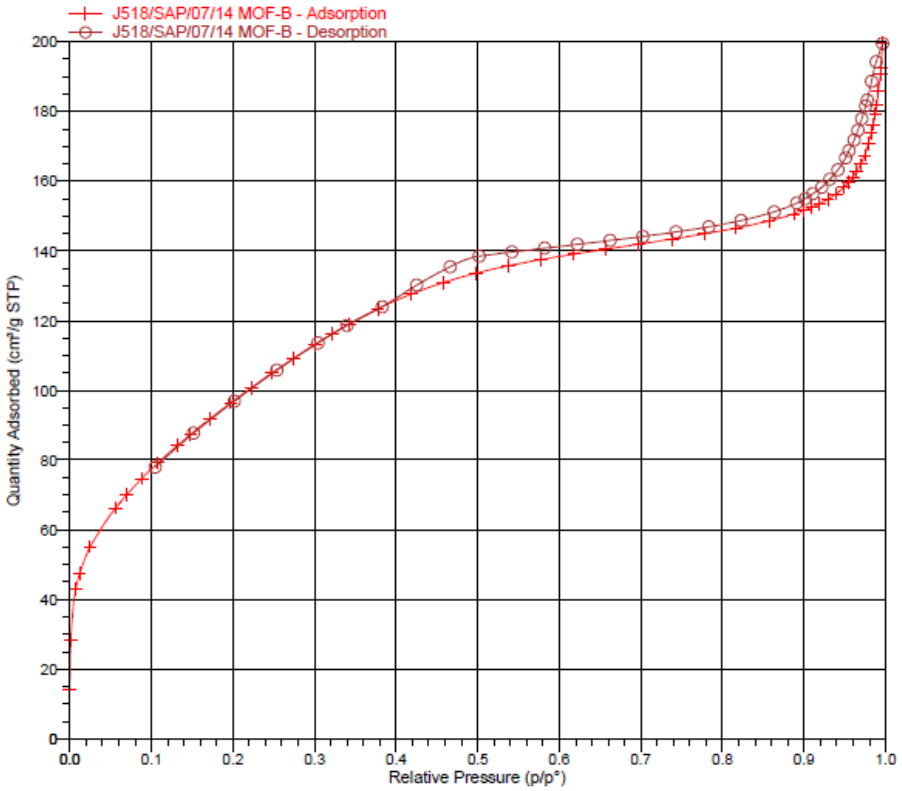

Figure 28: Isotherm Linear Plot for AM-MOF-235

From the figure above, it showed the type II isoterm. A type II is very different than the Langmuir model. The flatter region in the middle represents the formation of a monolayer. A type II isotherm is obtained when c > 1 in the BET equation. This is the most common isotherm obtained when using the BET technique. At very low pressures, the micropores fill with nitrogen gas. At the knee, monolayer formation is beginning and multilayer formation occurs at medium pressure. At the higher pressures, capillary condensation occurs.

The BET equation below, uses the information from the isotherm to determine the surface area of the sample, where X is the weight of nitrogen adsorbed at a given relative pressure (P/Po), Xm is monolayer capacity, which is the volume of gas adsorbed at standard temperature and pressure (STP), and C is constant. STP is defined as 273 K and 1 atm.

$$\frac{1}{X\left[\left({}^{P_0}/_{P}\right)-1\right]}=\frac{1}{X_mC}+\frac{C-1}{X_mC}\left(\frac{P}{P_0}\right)$$

Ideally five data points, with a minimum of three data points, in the P/P_0 range 0.025 to 0.30 should be used to successfully determine the surface area using the BET equation. At relative pressures higher than 0.5, there is the onset of capillary condensation, and at relative pressures that are too low, only monolayer formation is occurring. When the BET equation is plotted, the graph should be of linear with a positive slope. If such a graph is not obtained, then the BET method was insufficient in obtaining the surface area.

- The slope and y-intercept can be obtained using least squares regression.
- The monolayer capacity X_m can be calculated with equation below.

$$X_m=\frac{1}{s+i}=\frac{C-1}{Cs}$$

- Once X_m is determined, the total surface area S_t can be calculated with the following equation, where $L_{av}$is Avogadro's number, A_m is the cross sectional area of the adsorbate.

$$S=\frac{X_mL_{av}A_m}{M_v}$$

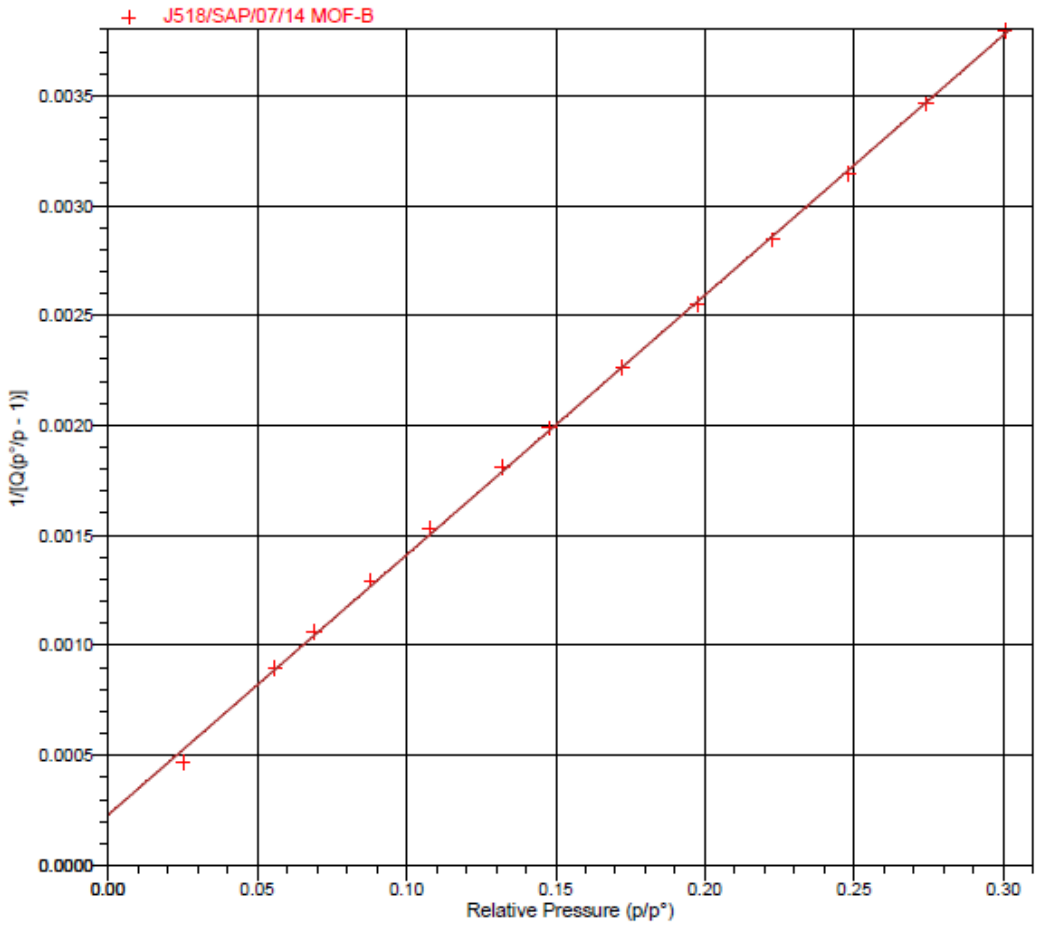

Figure 29: BET Surface Area Plot

Hence. Inserting the values into the equation above. The BET surface area of AM-MOF-235 can be calculated.

$$S = 361.91\ m^2g^{-1}$$

After amine modification, the nitrogen adsorption isotherm suggesting the occupation of the pore by amine. BET surface area of MOF-235 compared to AM-MOF-235 decreased to from 974 m^2g^{-1} to 361.91 m^2g^{-1} respectively, which confirms that AMP have occupied the channels and surfaces of MOF-235.

4.3 Carbon Dioxide Adsorption Capacity Results

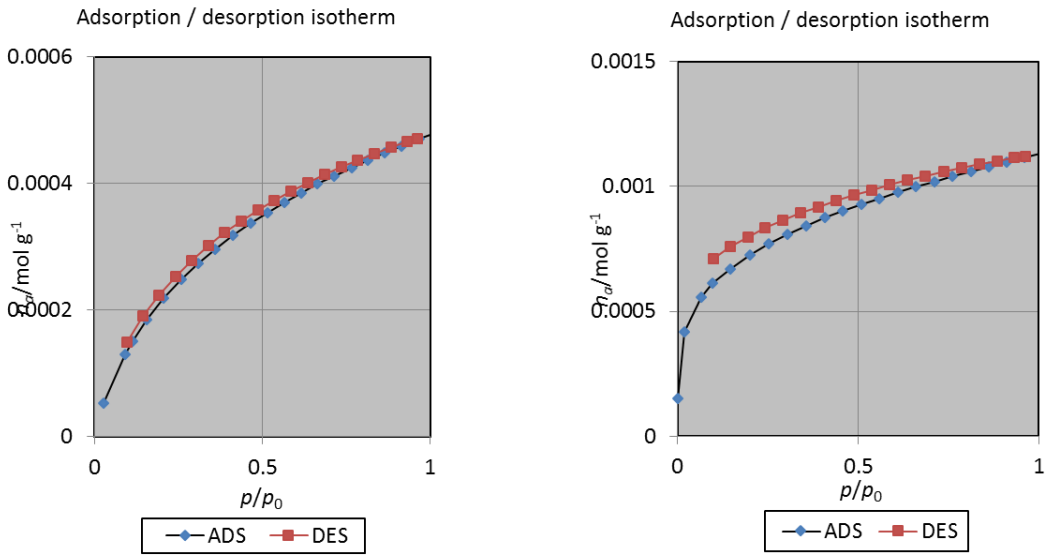

Figure 30: Left, MOF-235 CO_2 Adsorption Capacity. Right, AM-MOF-235 CO_2 Adsorption Capacity

The CO_2 adsorption capacity is being tested by using Belsorp Mini II at the $RCCO_2$ lab. When comparing the graphs, the adsorption capacity increase after being modified about 2.5 higher.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

In the nut shell, this project is important as it deals with alternative ways of reducing CO_2 emission to the atmosphere. MOF-235 is believed to be one of the effective ways to encounter the current problem with the conventional ways of capturing CO_2. The amine groups is grafted to enhance the rate of adsorption capacity of CO_2 into the pore. The project is within the capability of a final year student with the help from supervisor to be executed. The timeframe is feasible and the project can be completed within allocated time

From the characterization results, it is proven that the materials had been successfully synthesized. The crystallization successfully occurred and the BET surface area also gave a good results. The CO2 adsorption capacity also increased whem comparing both sample.

For the recommendations, the author would suggest to modify MOF-235 with different type of amines to study its effect. Plus, it is recommended to test MOF-235 with different type of gas adsoprtion capacity such as mehane and hydrogen.

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APPENDIX 1

IR Chart

Table of Characteristic IR Absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m–medium, w–weak, s–strong, n–narrow, b–broad, sh–sharp